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In Situ X-Ray Diffraction of the Delta to Alpha-Prime Transformation in Pu-Ga Alloys

K. J. M. Blobaum, J. R. Jeffries, M. A. Wall, H. Cynn, W. J. Evans, A. J. Schwartz

May 26, 2010

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In situ x-ray diffraction of the $\delta \rightarrow \alpha'$ transformation in Pu-Ga alloys
June 8, 2010

Kerri Blobaum, Jason Jeffries, Mark Wall, Hyunchae Cynn, William Evans & Adam Schwartz
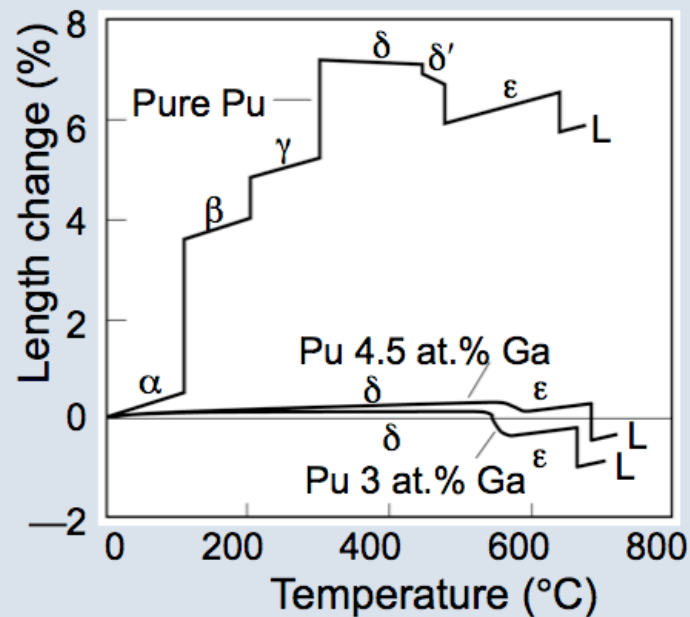
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The mechanisms and kinetics of the $\delta \rightarrow \alpha'$ transformation in Pu-Ga alloys remain unresolved
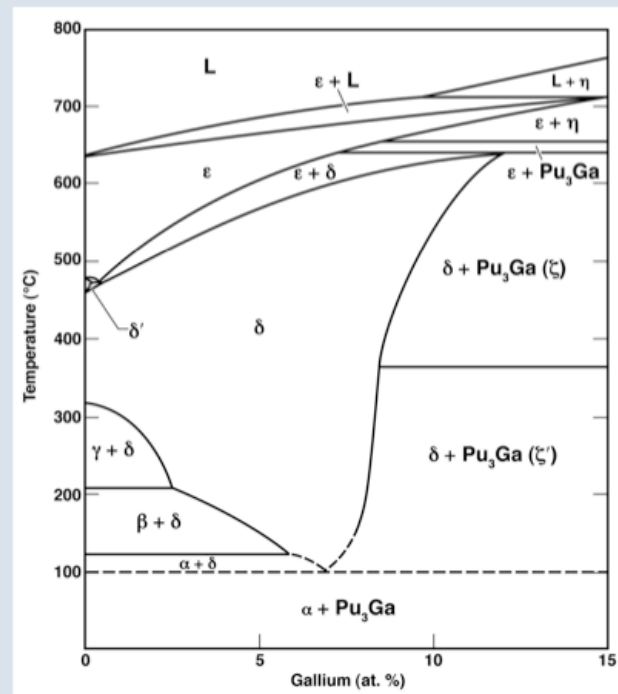
Unalloyed Pu

- **5 allotropic solid-solid transformations**

- **20% volume change between FCC δ phase and monoclinic α**

Hecker, *LA Science* (2000)

Equilibrium Thermodynamics

- **FCC δ phase in Pu-1.9 at.% Ga is metastable at ambient temperature**

- **At low T, δ transforms to metastable α' phase**

Schwartz *et al. Prog Mat Sci.* (2009)

# Upon cooling to sub-ambient temperatures, δ transforms to α′ via an isothermal martensitic transformation

Time-Temperature-Transformation diagram exhibits double-C curve kinetics

Orme *et al. Pu & Other Actinides* (1975)
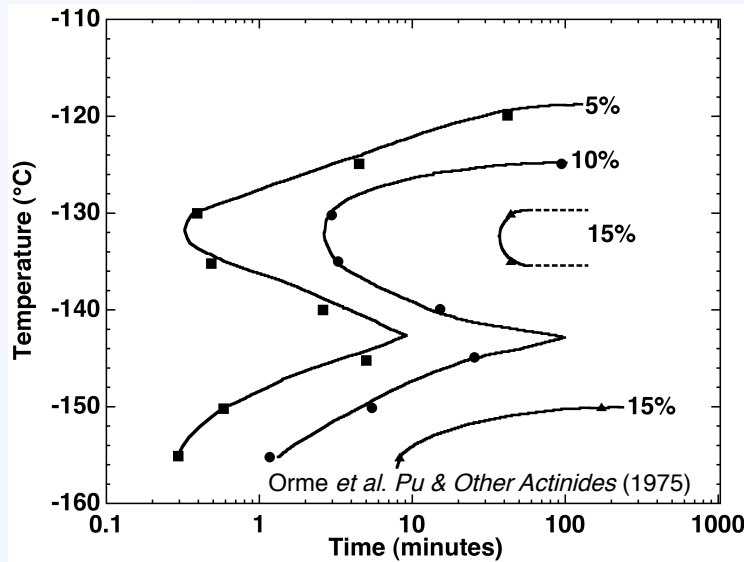
TTT diagrams of Pu-1.4 & 1.9 at.% Ga alloys show two separate knees

This observation implies two distinct, thermally activated mechanisms must exist for this transformation

The δ → α′ isothermal martensitic transformation can be induced with continuous cooling experiments
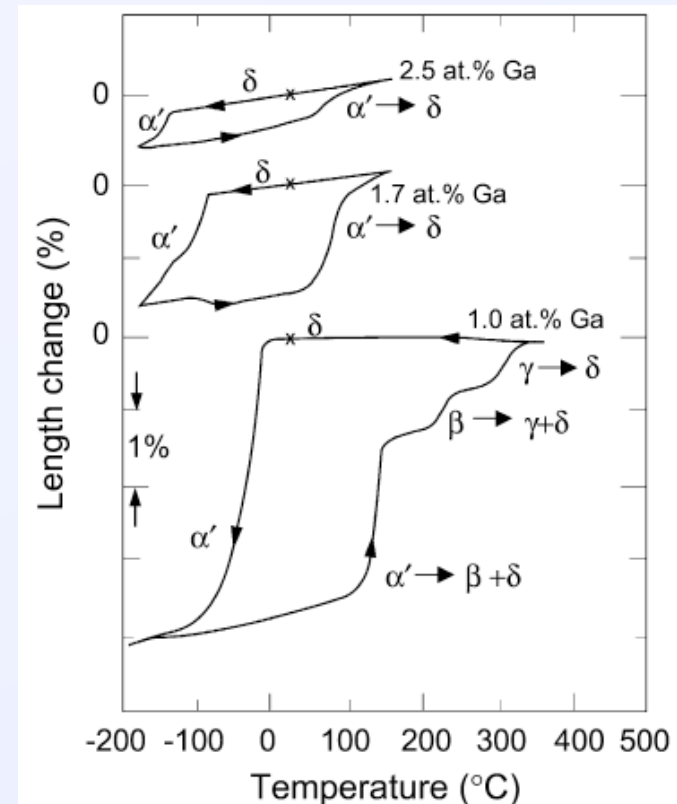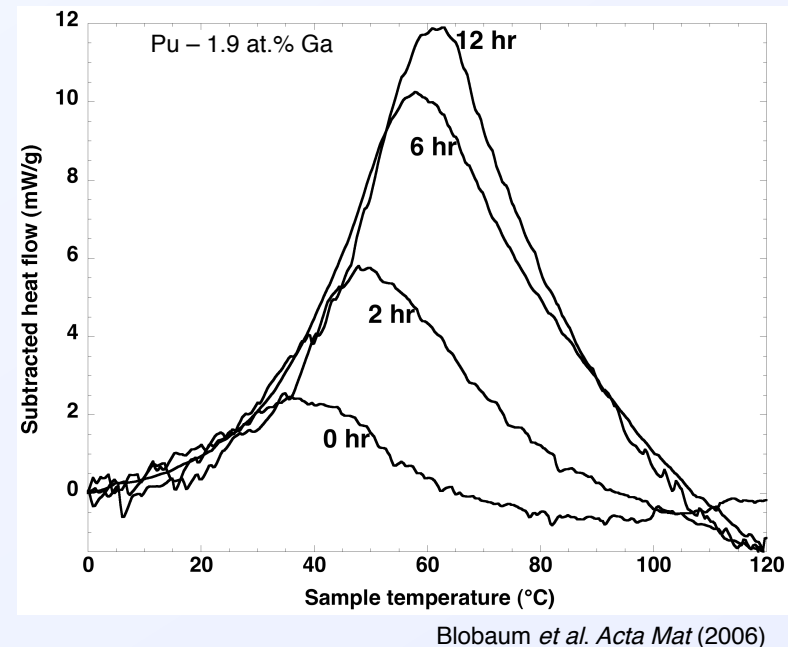

Hecker *et al. Prog Mat Sci.* (2004)

The amount of the $\delta \rightarrow \alpha'$ transformation is dependent on details of the thermal cycling and "conditioning"
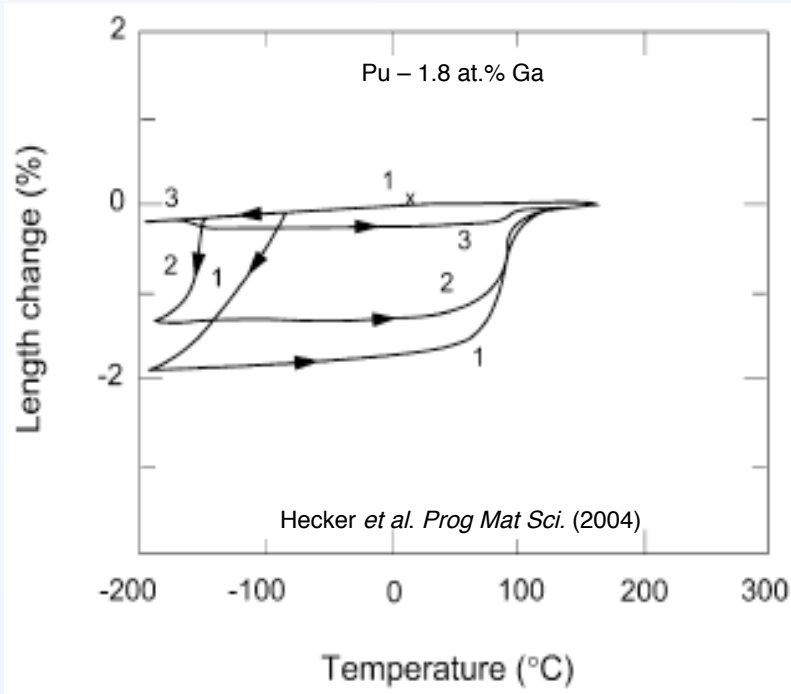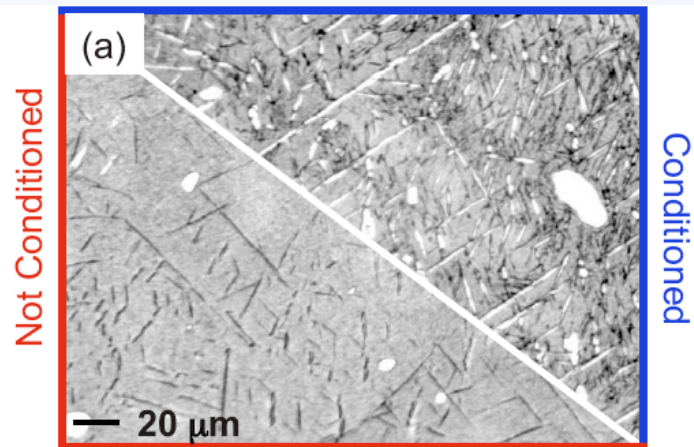

The amount of transformation in Pu – 1.8 at.% Ga alloys decreases with each thermal cycle
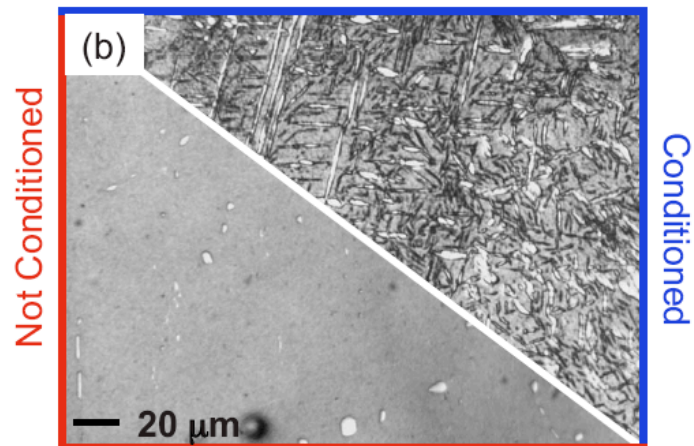

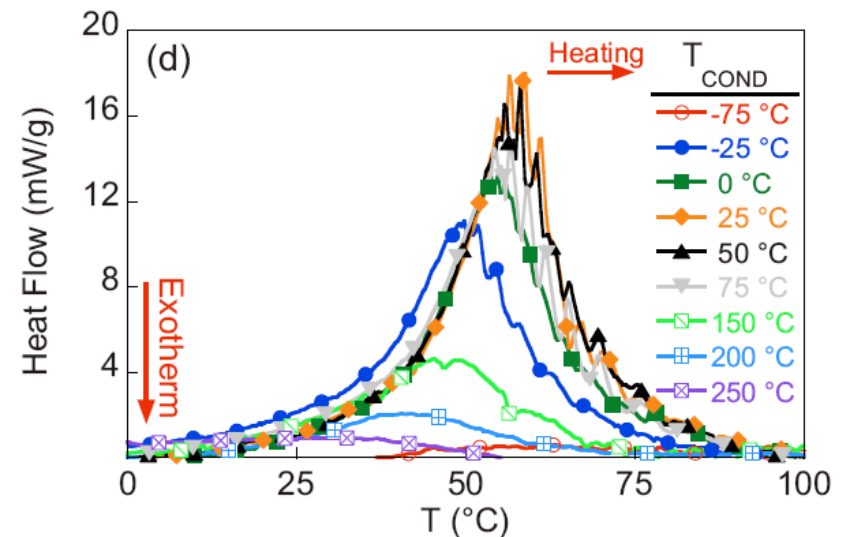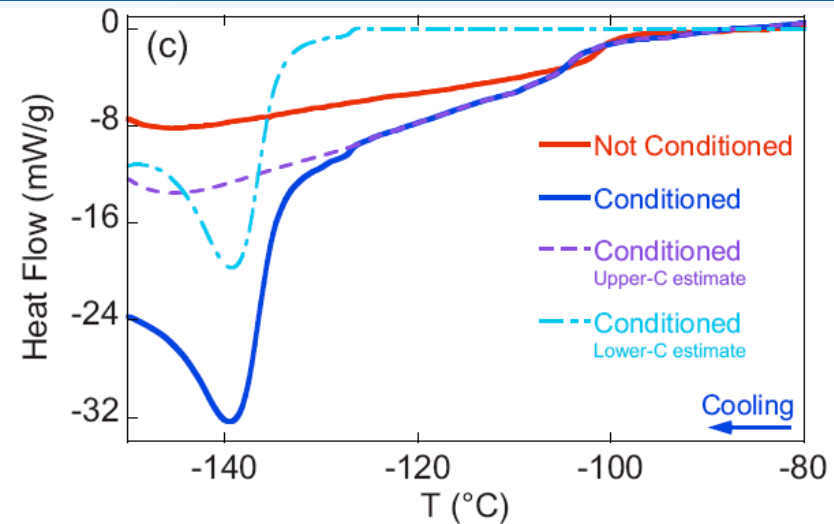Conditioning times of ~ 6 hours are required for reproducible amounts of transformation

A time-dependent process enhances $\delta \rightarrow \alpha'$ transformation at -120 °C and enables the transformation at −155 °C
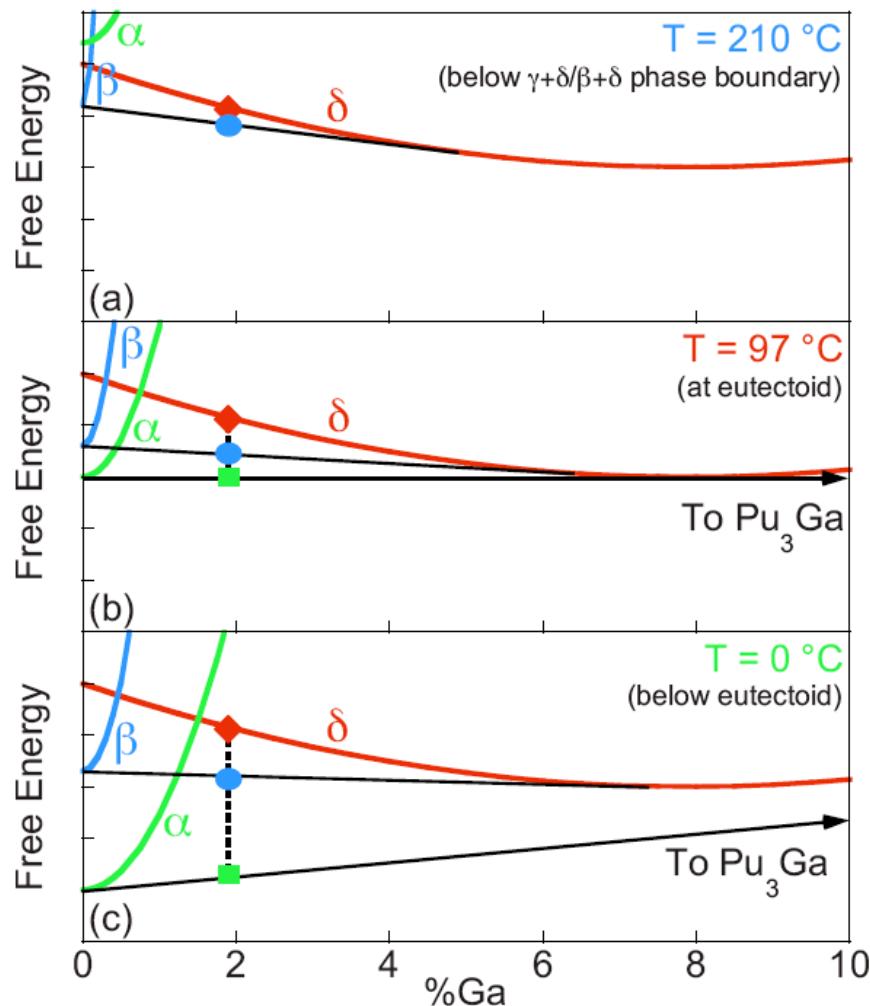

Jeffries *et al.* *PRB* (2009)
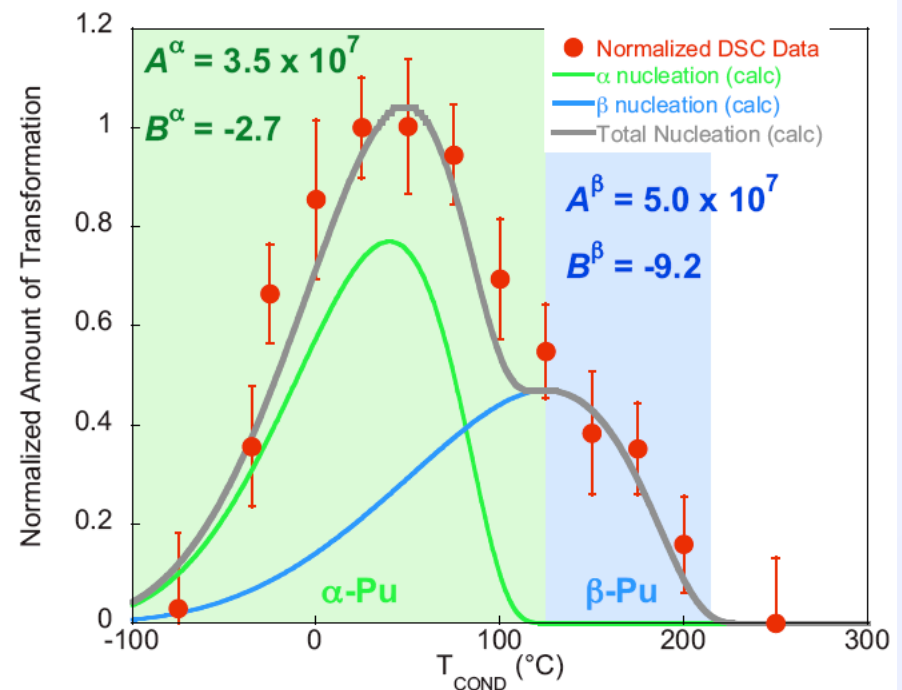
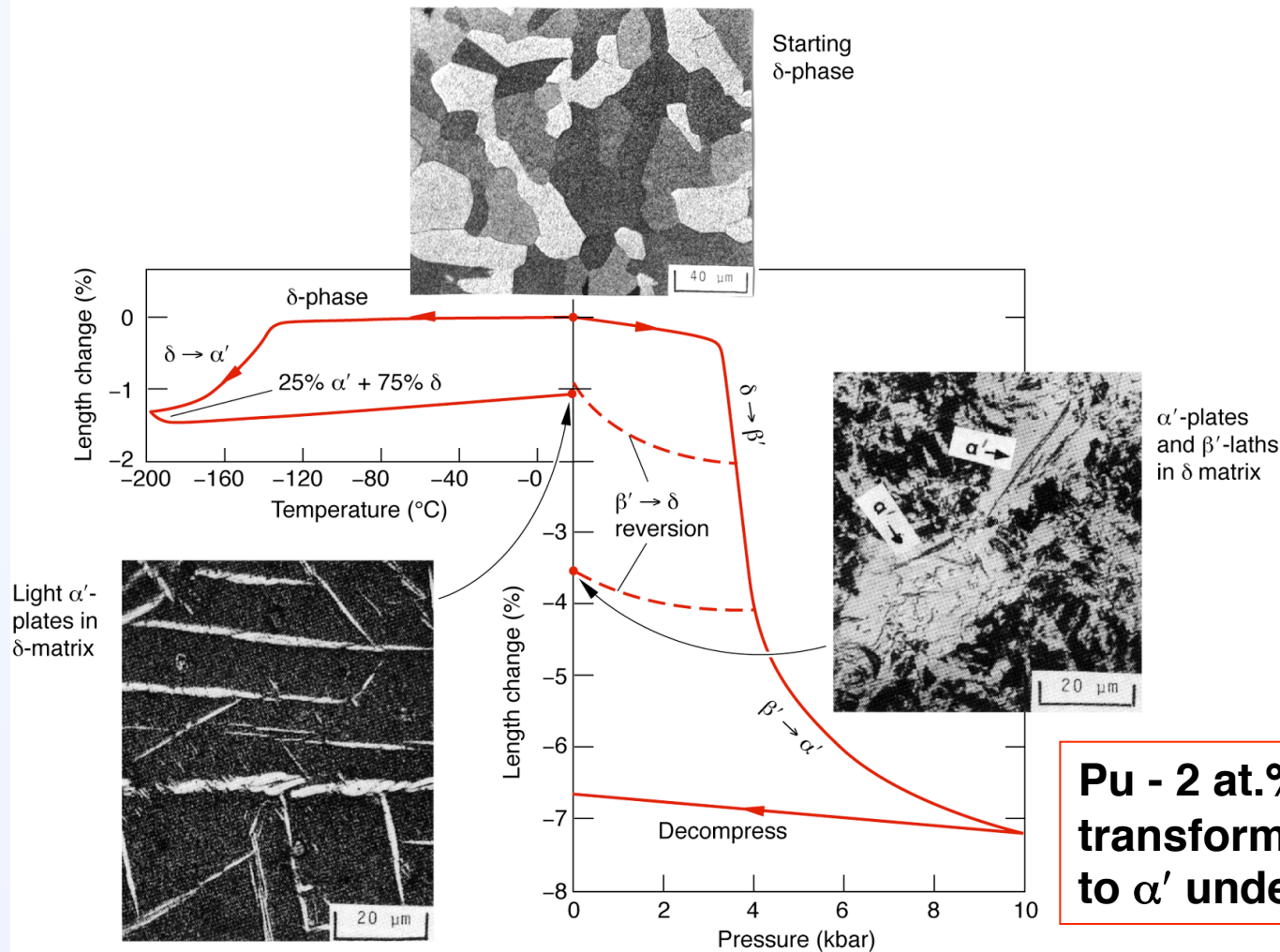# Nucleation of low Ga equilibrium phases may be the underlying mechanism of conditioning

Free energy – composition diagrams

Normalized amount of transformation as a function of conditioning temperature
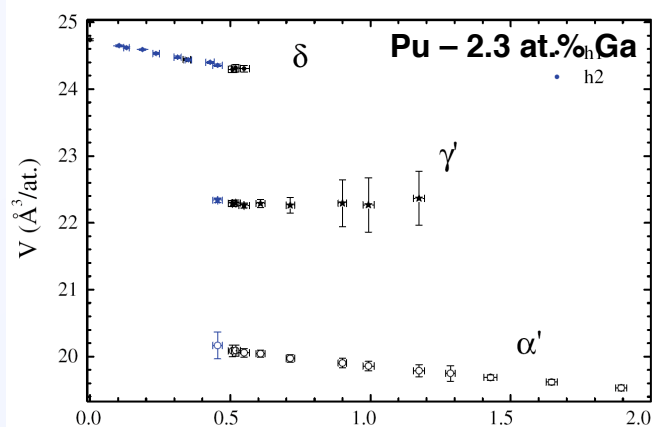
Jeffries *et al.* PRB (2009)

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The δ → α′ transformation can also be induced by pressure

Starting δ-phase

α′-plates and β′-laths in δ matrix
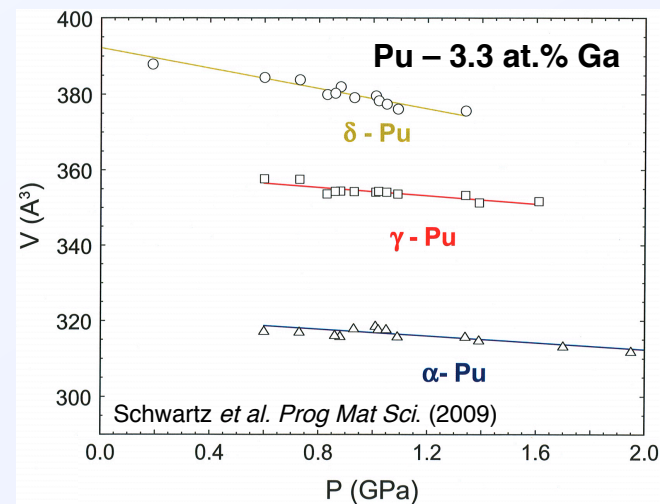
Light α′-plates in δ-matrix

Pu - 2 at.% Al alloys transform first to β′ then to α′ under pressure
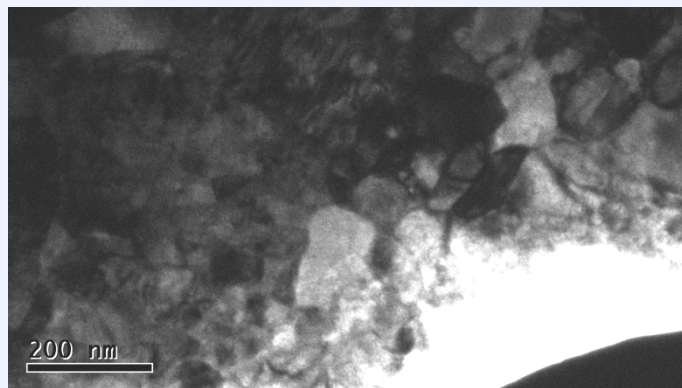
Hecker, *MRS Bulletin* (2001)

Diamond anvil cell experiments on Pu-Ga alloys reveal $\delta \rightarrow \gamma' \rightarrow \alpha'$ transformation sequence

Faure & Genestier *JNM* (2010)

Schwartz *et al. Prog Mat Sci.* (2009)

The pressure-induced transformation proceeds $\delta \rightarrow \gamma' \rightarrow \alpha'$; how about the isothermal martensitic transformation?

The isothermal $\delta \rightarrow \alpha'$ transformation was monitored *in situ* with XRD to probe for a γ' intermediate phase


- Advanced Photon Source at Argonne National Lab
- 90 μm x 90 μm spot size, rastered
- 15°C/min cooling rate + isothermal hold (-120°C, -155°C)
- 8 second collection time for XRD patterns
- Transmission geometry
- Well-homogenized sample, ~30 μm grain size
- Pu-1.9 at.% Ga alloy, 30 – 80 μm thick

3.1"

Triple-encapsulation sample holder
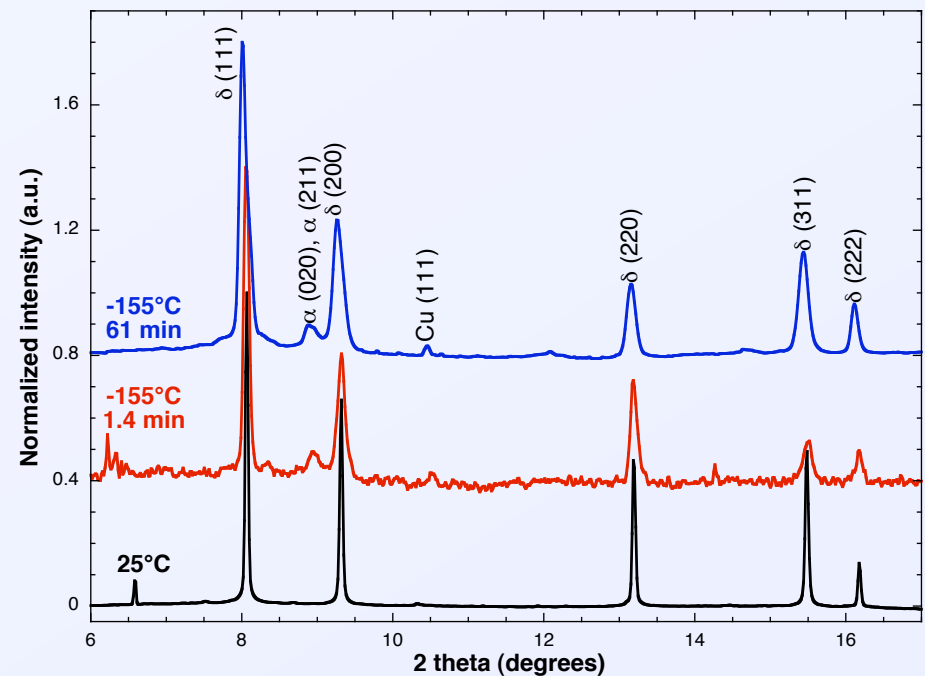designed for transmission x-ray diffraction
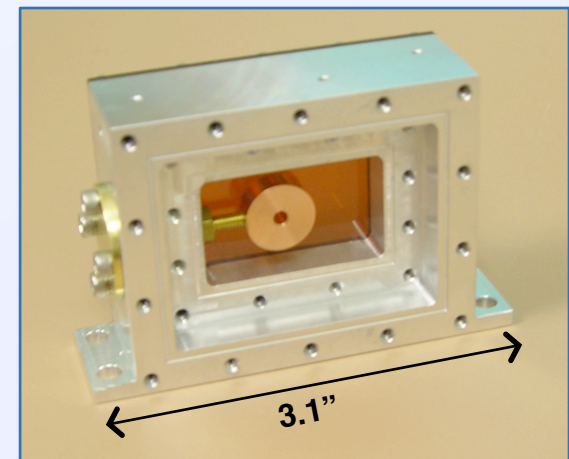
δ → α′ transformation was observed at both C-curve temperatures, even in a 30 μm thick sample

-120°C (Upper-C curve)
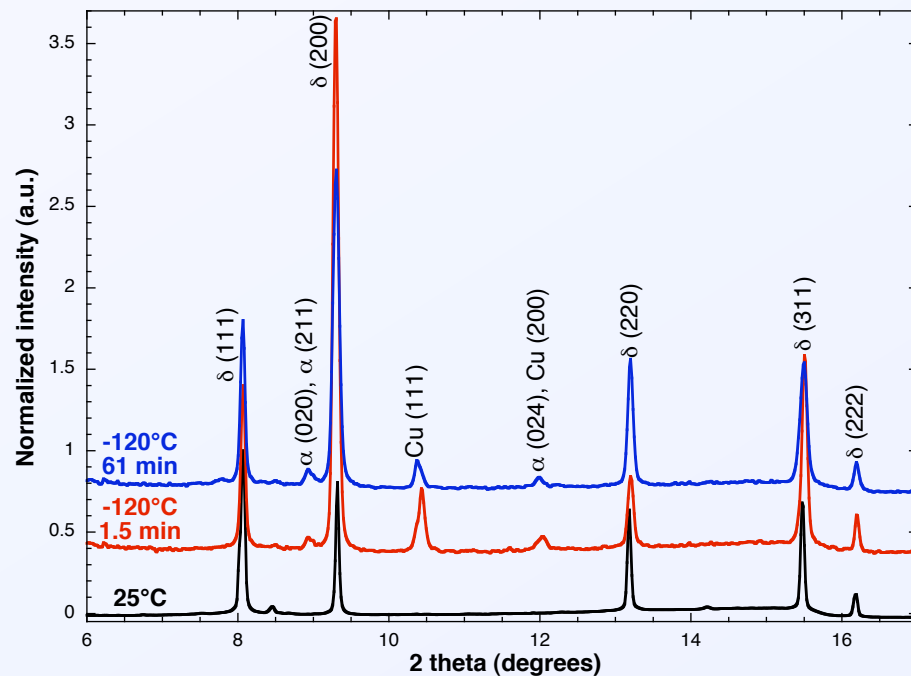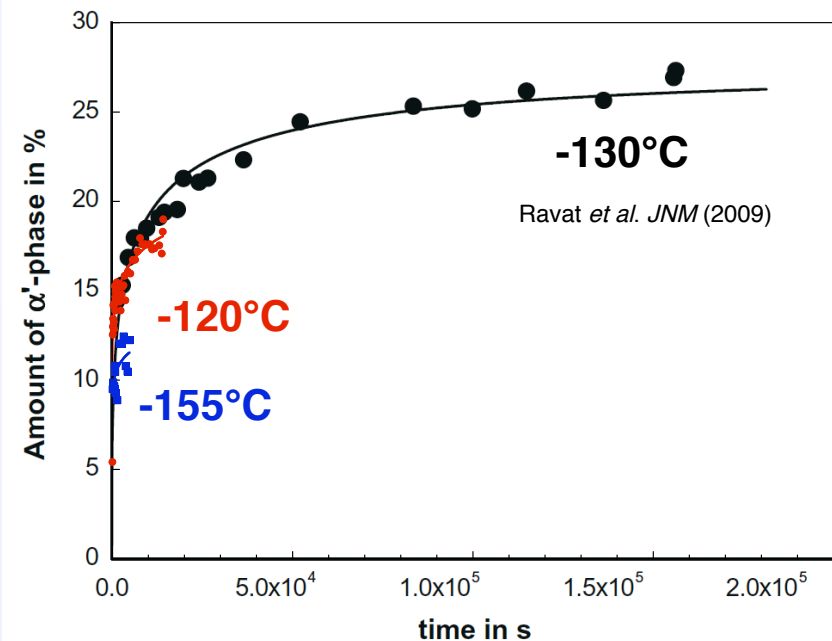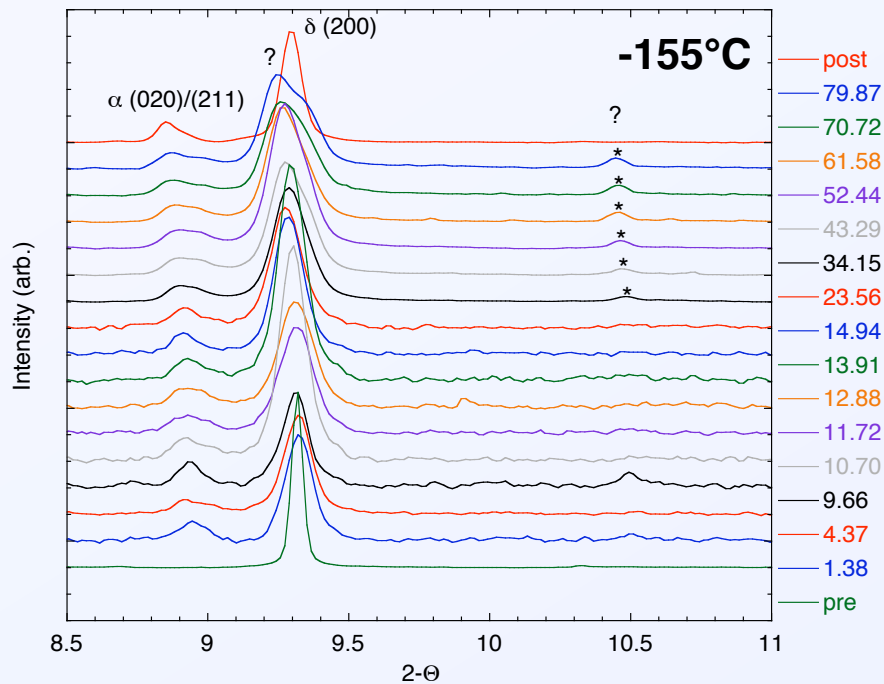
-155°C (Lower-C curve)

The majority of the α' phase forms quickly, and it continues to grow in for several hours

The onset of α' formation and transformation rate correlate well with data in the literature
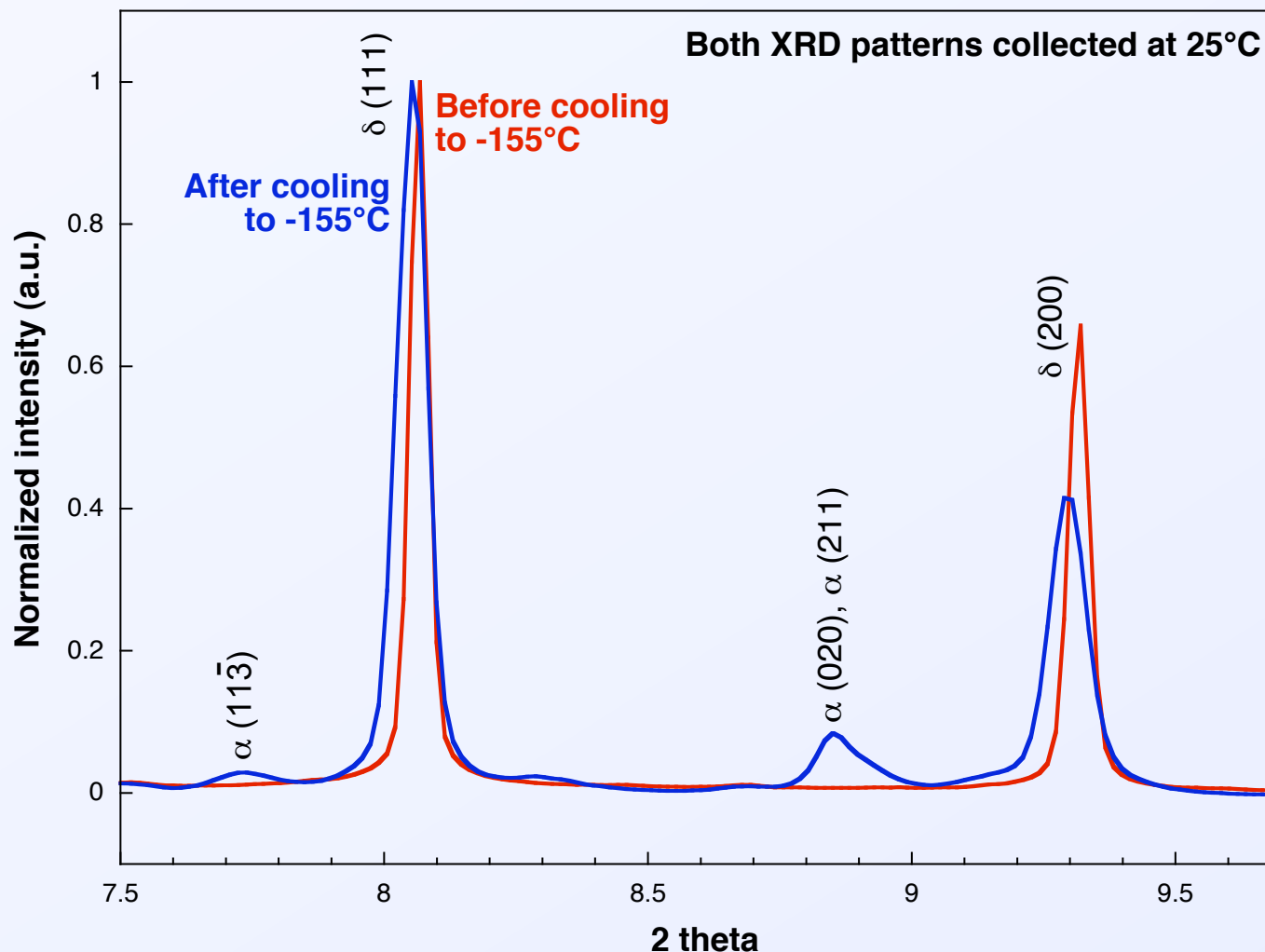
The δ lattice parameter increases to accommodate formation of the α′ phase

- Density of α′ is 24% higher than δ
- Formation of α′ causes significant elastic and plastic deformation in the δ lattice
- Expansion is greater at -155°C than at -120°C
- -120°C: 0.2% expansion after 90 minutes
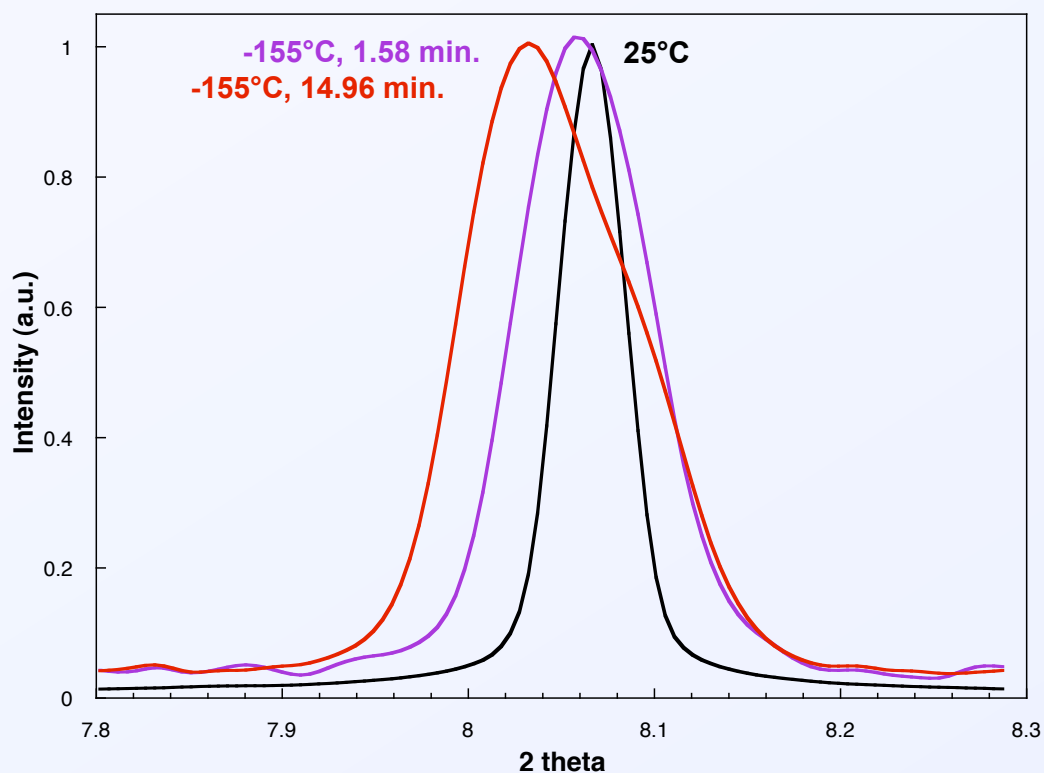- -155°C: 0.35% expansion after 80 minutes
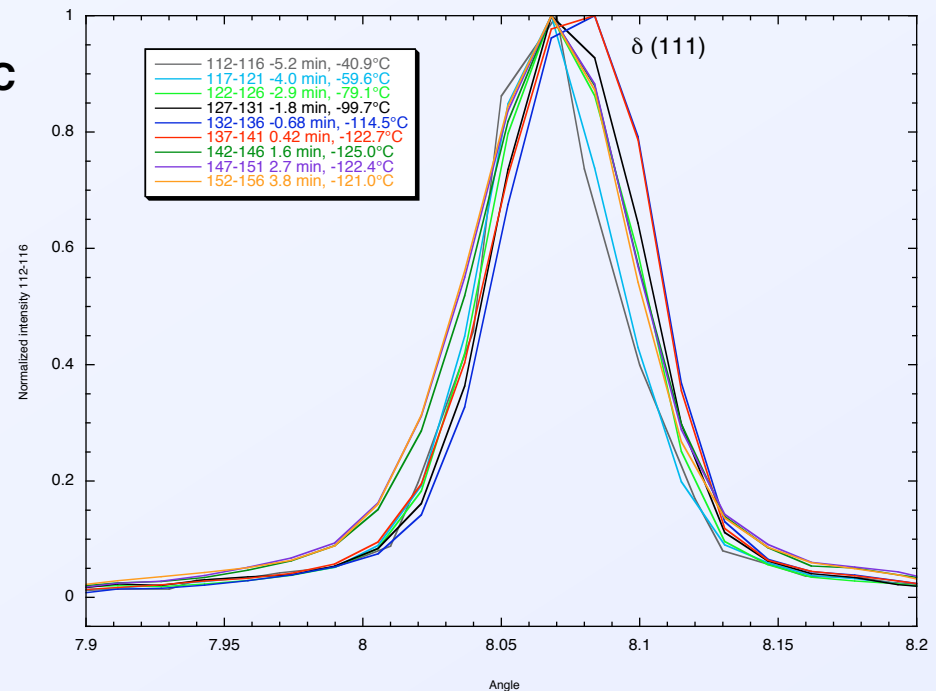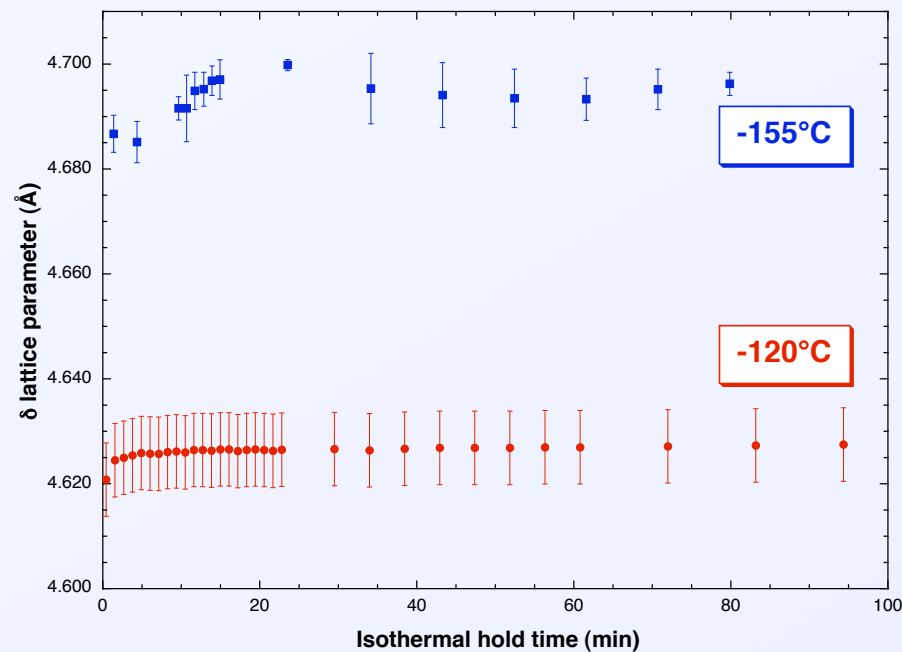
The onset of α′ formation is evidenced by a shift in the δ (111) peak position
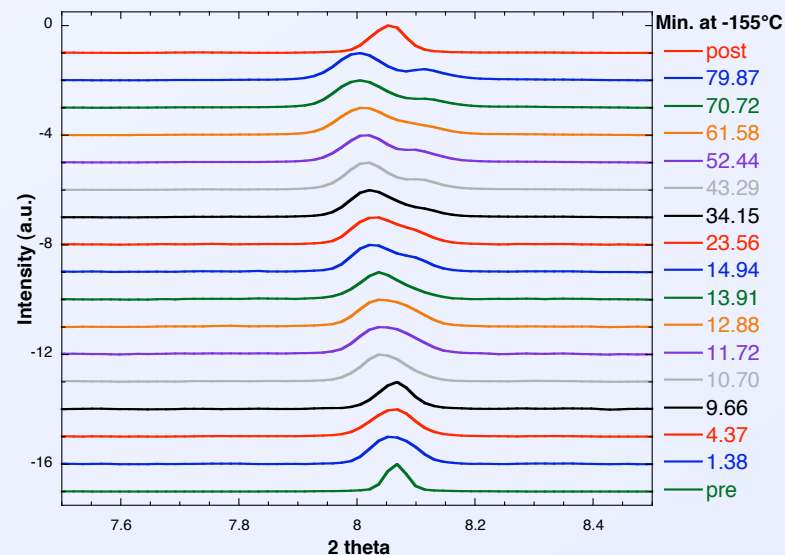
After α′ forms, the δ lattice parameter does not return to its pre-transformation value at 25°C
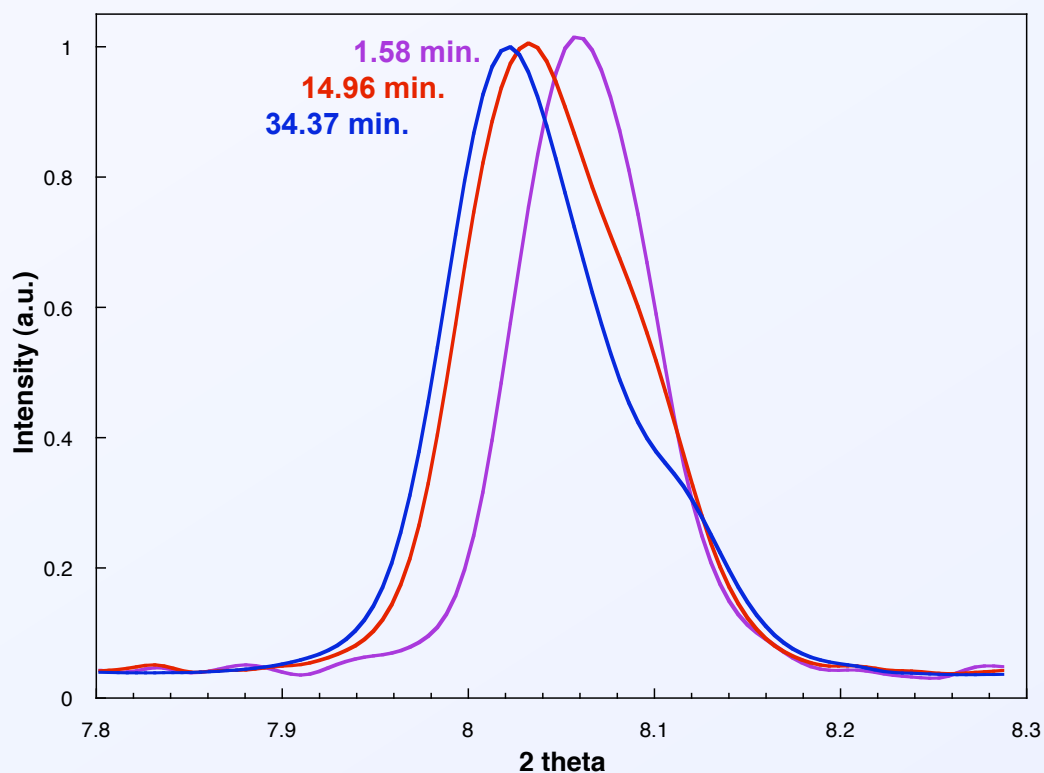
At -155°C, a shoulder grows on the δ (111) peak

- A shoulder is evident after ~15 minutes
- Becomes a distinct peak after ~43 minutes
- This secondary peak disappears when the sample is reheated to 25°C
- Origin of this peak is unknown
- Tetragonal distortion of the δ lattice?

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At -155°C, a shoulder grows on the δ (111) peak

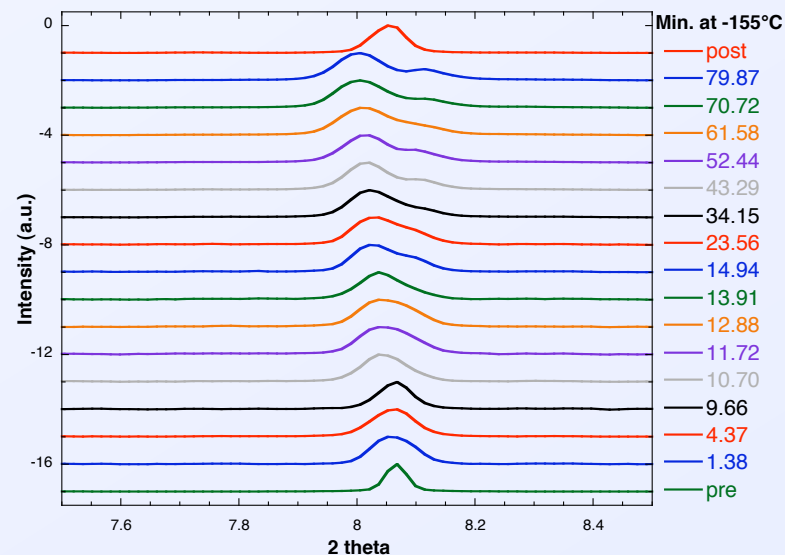

1.58 min.
14.96 min.
34.37 min.

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14.96 min.
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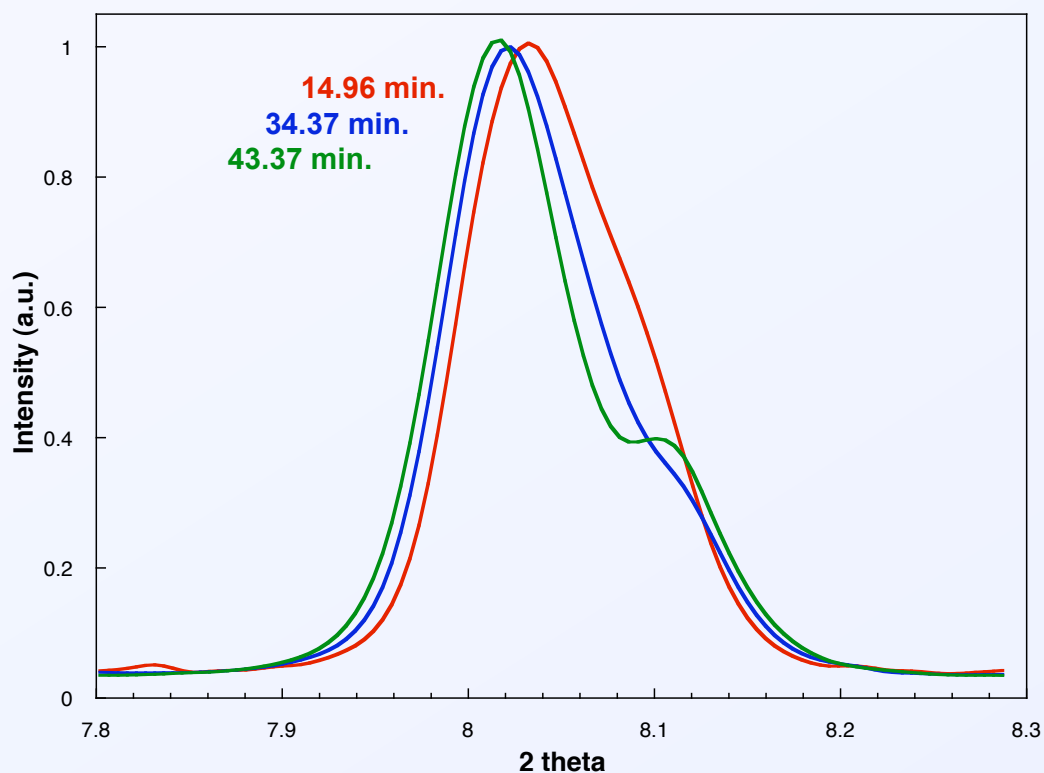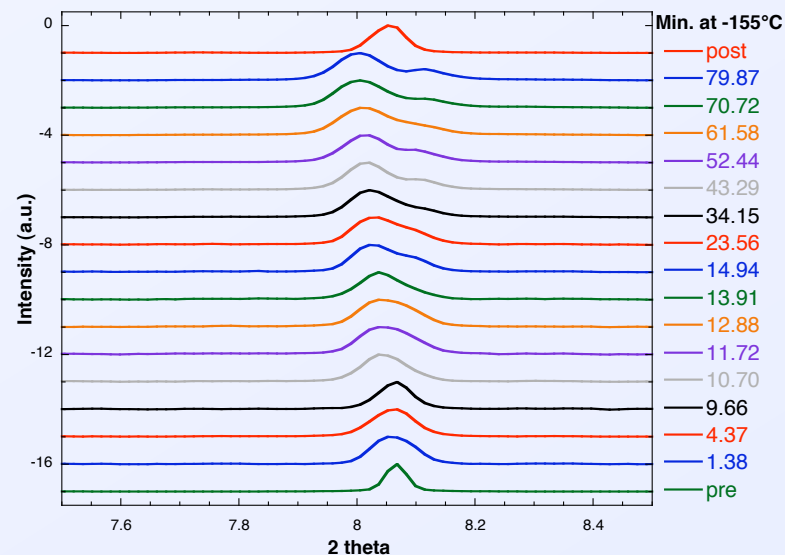**Lawrence Livermore National Laboratory**
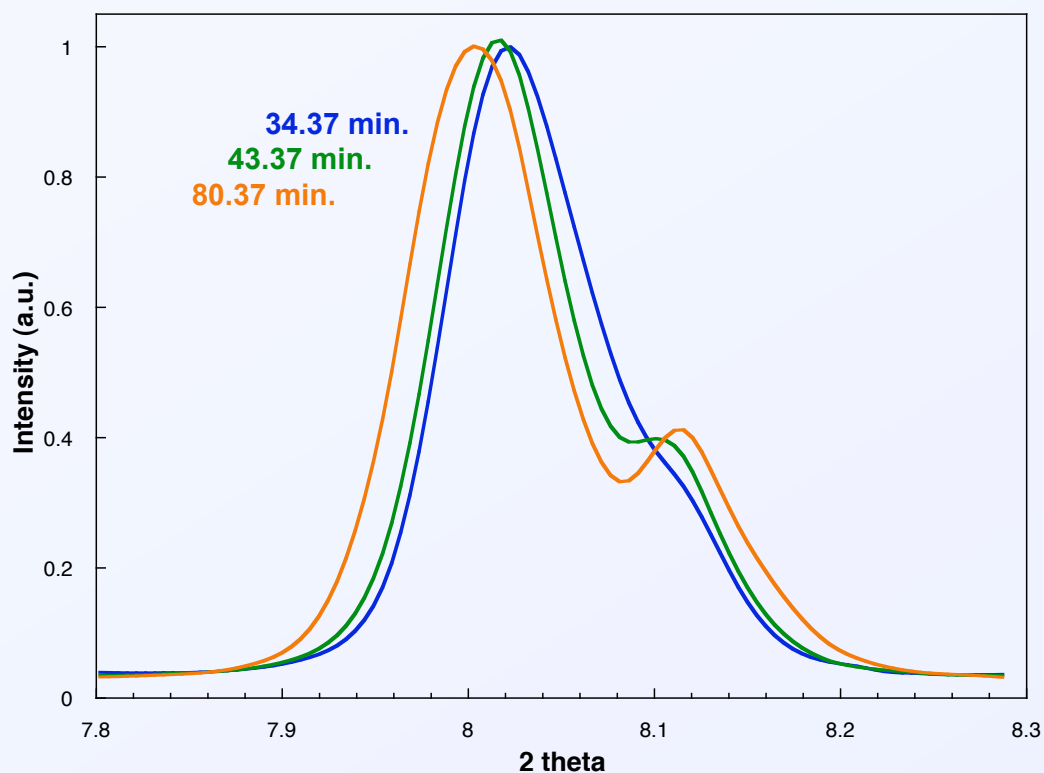
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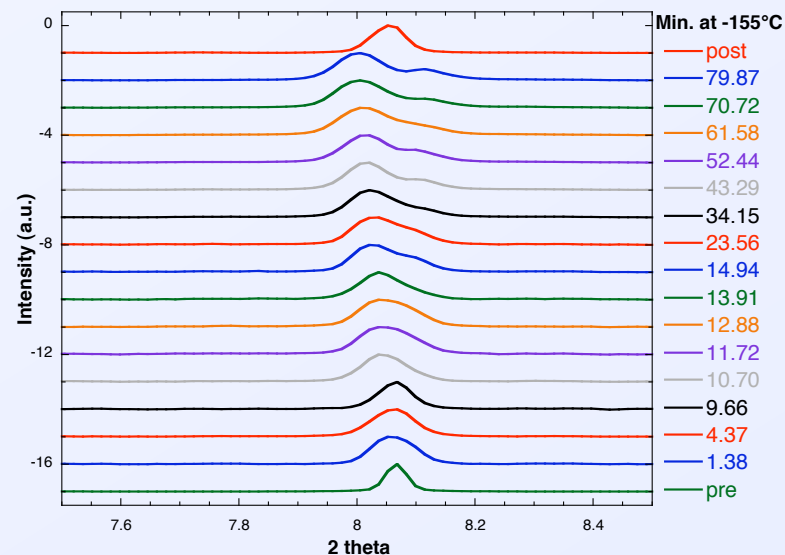# At -155°C, a shoulder grows on the δ (111) peak

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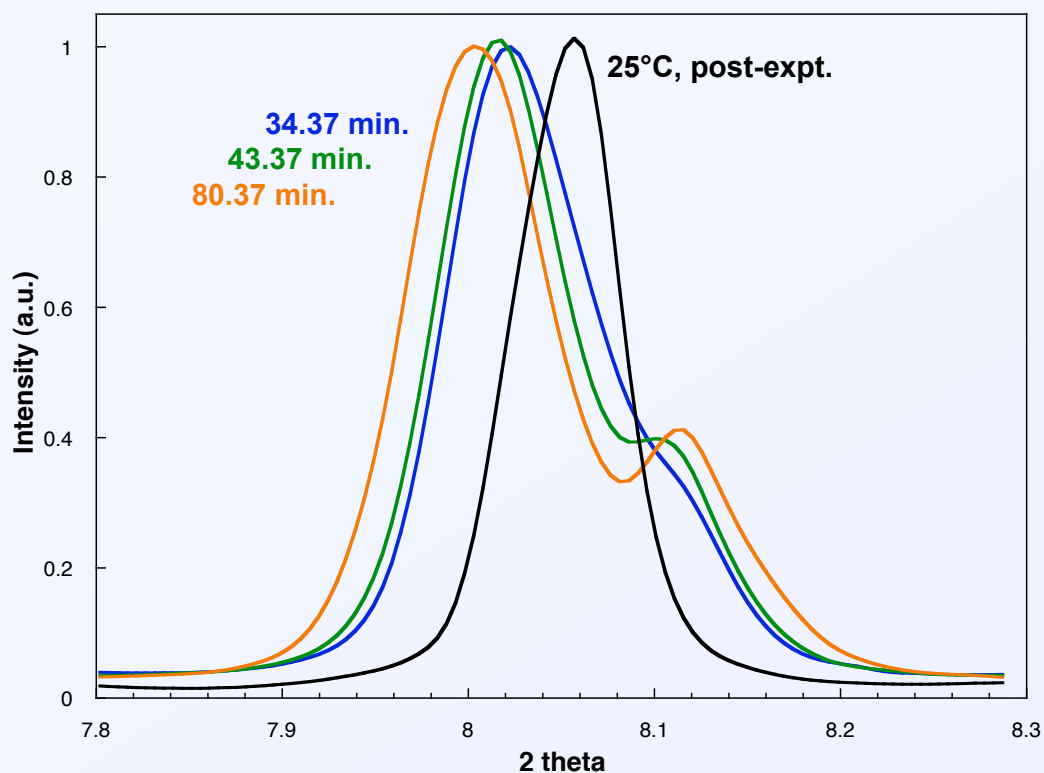- Tetragonal distortion of the δ lattice?

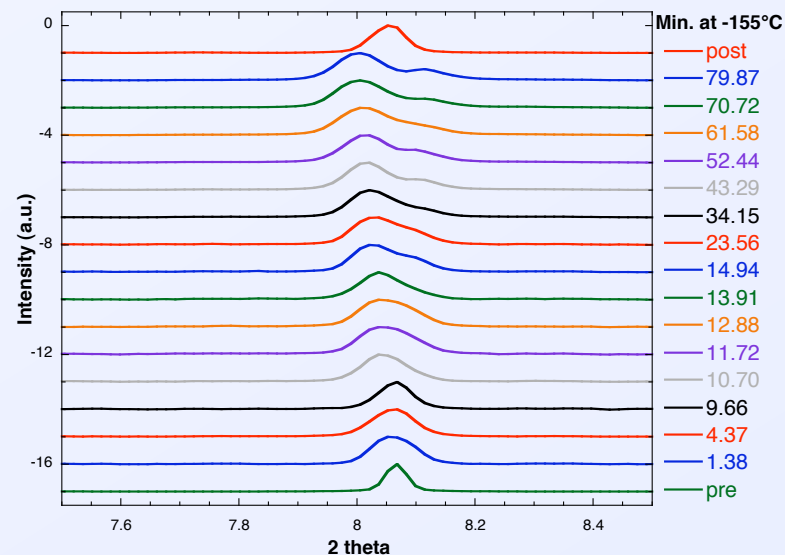# At -155°C, a shoulder grows on the δ (111) peak

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Conclusions

- γ' is not observed as an intermediate in the $\delta \rightarrow \alpha'$ transformation (Pu-1.9 at. % Ga alloy)
- The double-C curve kinetics are not the result of intermediate phase formation
- The δ lattice parameter expands to accommodate the α' phase
- Formation of a secondary peak on the $\delta(111)$ peak at -155°C was identified
  - Origin of this peak remains unknown
- XRD experiments will be repeated with a lower-Ga alloy in the future

Isothermal: –155°C/4 hours

25 μm

Pressure-induced: 1 GPa

200 nm

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